

In the Claims

81. (Withdrawn): An initiator for ATRP polymerization having the general formula:



wherein the core molecule Y comprises a small molecule or a macromolecule, a soluble or insoluble, organic, inorganic or composite molecule,

X is radically transferable atom or group, and

n is the number of radically transferable atoms or groups on the core molecule.

82. (Withdrawn): The initiator of Claim 81, wherein Y comprises an organic molecule which comprise soluble, swellable, or insoluble molecules, a synthetic molecule or a natural-based material, crosslinked support or other organic materials initially containing one or more functional group(s) that are or can be substituted by known chemical processes to form group(s) containing one or more radically transferable atoms or groups.

83. (Withdrawn): The initiator of Claim 82, wherein the organic molecule comprises a synthetic molecule or natural-based material.

84. (Withdrawn): The initiator of Claim 83, wherein the natural-based material is selected from the group consisting of cellulose, glucose, cotton, wool, and derivatives thereof, and wherein the natural-based material is soluble or insoluble in a reaction media.

85. (Withdrawn): The initiator of Claim 82, wherein the organic molecule initially comprises at least one functional group selected from the group consisting of a hydroxy, thiol, amine, amide, and mixtures thereof.

86. (Withdrawn): The initiator of Claim 81, wherein Y is the biodegradation product of a biodegradable polymer.

87. (Withdrawn): The initiator of Claim 81, wherein Y may be fragmented in a recycling process for the recovery of reusable polymer segments.

88. (Withdrawn): The initiator of Claim 81, wherein Y may be degraded by moisture in a process for the preparation of repulpable polymers.

89. (Withdrawn): The initiator of Claim 81, further comprising an inorganic molecule or an inorganic surface which initially contains functional groups or derivatives thereof that contain one or more radically transferable atoms or groups or functional groups.

90. (Withdrawn): The initiator of Claim 81, wherein Y comprises a silica surface, a siloxane cube or a cyclotriphosphazene ring.

91. (Currently Amended): A macroinitiator for ATRP polymerization of free radically (co)polymerizable monomers, comprising:
~~a polymer block comprising ring opening polymerizable monomeric units derived from ring opening (co)polymerization of cyclic monomers or oligomers, and at least one comprising a free radically transferable atom or group as a substituent chemically bonded to the polymer block.~~

92. (Cancelled).

93. (Cancelled).

94. (Currently Amended): A polyphosphazene multifunctional macroinitiator for an ATRP (co)polymerization, comprising: a polymer block comprising ~~cyclic hexachlorotriphosphazene monomer units, and monomeric units derived from a ring-opening polymerization of cyclic hexachlorotriphosphazene followed by a reaction with at least one nucleophile containing radically transferable atoms of or groups chemically bonded to the polymer block.~~

95. (Cancelled)

96. (Withdrawn): A supported initiator for ATRP polymerization, formed by treating a surface with a molecule comprising a first functionality capable of reacting with said

surface and a second functionality comprising one or more radically transferable atoms or groups.

97. (Withdrawn): The supported initiator of Claim 96, wherein the surface is an inorganic surface.

98. (Withdrawn): The supported initiator of Claim 96, wherein the surface is an organic surface.

99. (Withdrawn): A supported initiator of Claim 97, wherein the inorganic surface is a silica surface and the molecule comprises a substituted silane.

100. (Amended): A macroinitiator for ATRP, comprising a polymer block comprising at least one of radically polymerizable monomer unit, and monomeric units derived from a polymerization in the presence of a transfer agent, wherein the transfer agent comprises at least one transfer agent chemically bonded to the polymer block, wherein the transfer agent comprises a radically transferable atoms or groups.

101. (Currently Amended): A polyvinyl acetate macroinitiator for ATRP, comprising a polymer block comprising vinyl acetate monomer units, and monomeric units derived from a polymerization in the presence of a chain transfer agent, wherein the chain transfer agent comprises at least one transfer agent chemically bonded to the polymer block, wherein the transfer agent comprises a radically transferable atom or group.

102. (Currently Amended): A macroinitiator for ATRP, comprising a polymer block comprising living anionic polymerizable monomer units, and monomeric units derived from a living anionic polymerization, wherein the polymerization is quenched with a molecule comprising at least one radically transferable atom or group chemically bonded to the polymer block.

103. (Currently Amended): A macroinitiator for ATRP of free radically (co)polymerizable monomers, comprising a polymer block comprising living cationic polymerizable

monomer units derived from a living cationic polymerization of styrene; and -a radically transferable atom or group bonded to on at least one styrene terminus termini.

104. (Currently Amended): A polyolefin (co)polymer macroinitiator, comprising a polyolefin (co)polymer block; and a radically transferable atom or group chemically bonded to the polymer block.

105. (Currently Amended): The polyolefin (co)polymer macroinitiator of Claim 104, wherein the radically transferable atom or group is at least one of comprising one of a halogen and a sulfonyl halide.

106. (Currently Amended): An initiator for the preparation of a "bottle brush" or comb shaped (co)polymer, comprising a ~~a~~ polymer block comprising radically polymerizable monomer units, and monomeric units derived from a linear polymerization of a monomer comprising a radically transferable atom or group, and at least one radically transferable atom or group chemically bonded to residing on each monomer unit.

107. (Currently Amended): An initiator for the preparation of a "bottle brush" or comb shaped, or graft (co)polymers, comprising a polymer block comprising radically polymerizable monomer units, monomeric units derived from a linear (co)polymerization of a monomer containing a radically transferable atom or group with a second comonomer; and at least one radically transferable atom or of groups chemically bonded to the polymer block.

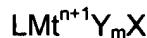
108. (Currently Amended): A multifunctional initiator for an ATRP polymerization to give a "bottle brush" or comb shaped (co)polymer, comprising a polymer block comprising radically polymerizable monomeric units derived from a linear polymerization of a monomer containing a functional group; and at least one group containing at least one radically transferable atom or group chemically bonded to the polymer block, wherein

the multifunctional initiator is a polymer with one or more radically transferable atoms or groups on each radically polymerizable monomeric unit.

109. (Cancelled).
110. (Currently Amended): A multifunctional macroinitiator for preparation of a block copolymer, comprising with one or more "bottle brush" block(s), wherein at least one of the blocks in said block copolymer is prepared from a monomer containing a radically transferable group, or a group that can be converted to a group containing and a plurality of radically transferable atoms or groups chemically bonded to the polymer block.
111. (Withdrawn): An initiator for a controlled polymerization process, which can be isolated or used in-situ, for the polymerization of free radically (co)polymerizable monomers, formed by the capture of a (functional)-free radical having the structure:



by reaction with a transition metal compound of the structure:



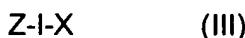
wherein Z is any functional group, including non-reactive groups, that does not interact during an ATRP polymerization process,

Mt^{n+1} is a reaction metal in the oxidation state $n+1$, wherein and X is a radically transferable counterion,

Y_m may either be the same as X, a radically transferable counterion different from X, or a non-transferable counter ion, and

in the presence of solubilizing ligand(s) L,

wherein X is transferred from the metal compound to the free radical, creating a molecule of structure (III),



that can be isolated, or directly used as an initiator for controlled free radical (co)polymerization of monomers, optionally present in the system, through a catalyzed redox reaction with the metal compound now converted into a metal compound of lower oxidation state having the structure:



wherein Mt, X and Y are defined as above, and

I^* is a substituted C, S, O, N, P, Sn, or any other atom that can form a free radical by any process.

112. (Withdrawn): The initiator Claim 111, wherein the said free radical is first formed by the decomposition of an organic peroxide, organic persulfate, inorganic persulfates, peroxydisulfate, azocompounds, peroxycarbonates, perborates, percarbonates, perchlorates, peracids, hydrogen peroxide, and mixtures thereof, optionally containing a functional group that does not interact in ATRP.
113. (Withdrawn): The process of Claim 111, wherein the transition metal complex is chosen to render the polymerization system homogenous.
114. (Withdrawn): The process of Claim 111, wherein the monomers include substituted or unsubstituted acrylates, methacrylates, (meth)acrylamides and (meth)acrylonitriles.
115. (Withdrawn): The process of Claim 111, wherein one or more of the radically transferable atom(s) or group(s) present on the transition metal complex in its higher oxidation state is a halogen.
117. (Withdrawn): A multifunctional polymerization initiator compound, comprising:
 - at least one radically transferable atom or group capable of initiating an atom transfer radical polymerization; and
 - at least one initiation group capable of initiating at least one of a cationic, an anionic, a peroxide initiated free radical, a controlled free radical, metathesis, ring

opening and coordination polymerization process.

118. (Withdrawn): The multifunctional polymerization initiator compound of claim 117, wherein the at least one initiation group comprises a peroxide group.
119. (Currently Amended): A macroinitiator for polymerization processes, comprising:
 - a free radical polymerization initiator group comprises comprising at least one of an azo group and a peroxy group; and
 - at least two polymer blocks each comprising methacrylate monomeric units attached to the conventional free radical polymerization initiator group.
120. (Currently Amended): A macroinitiator for polymerization processes, comprising:
 - a polymer block comprising radically polymerizable monomers; and
 - a free radical polymerization initiation group chemically bonded to the polymer block.
121. (Currently Amended): The macroinitiator for polymerization processes of claim 120, wherein the polymer block comprises monomer units derived from dimethyl aminomethyl methacrylate monomer units monomers.

122. (Currently Amended): A macroinitiator for polymerization processes, comprising:

a polymer block, comprising at least one monomer unit derived from monomers capable of being polymerized by a process selected from the group consisting of cationic, anionic, free radical, controlled free radical, metathesis, ring opening, and coordination polymerization processes; and

at least one radically transferable atom or group capable of initiating an atom or group transfer radical polymerization chemically bonded to the polymer block.

123. (Currently Amended): The macroinitiator for polymerization processes of claim 122, wherein the monomers units are derived from at least one of a styrene, a vinyl chloride, and a vinyl acetate; and further comprising a second polymer block comprising monomers units derived from at least one monomer selected from the group consisting of substituted styrene(s), (meth)acrylates, (meth)acrylonitrile, (meth)acrylamides, and other radically polymerizable monomers capable of being polymerized by an atom or group transfer radical polymerization.

124. (Withdrawn): A macroinitiator for polymerization processes, comprising:

a polymer block;

at least two radically transferable atoms or groups capable of initiating an atom or group transfer radical polymerization process; and

at least one initiation group capable of initiating a free radical polymerization process.

125. (Withdrawn): The multifunctional polymerization initiator compound of claim 117, wherein the radically transferable atoms or groups comprise:

Cl, Br, I, OR¹⁰, SR¹⁴, SeR¹⁴, OP(=O)R¹⁴, OP(=O)(OR¹⁴)₂, OP(=O)OR¹⁴, O-N(R¹⁴)₂ and S-C(=S)N(R¹⁴)₂, where R¹⁰ is alkyl of from 1 to 20 carbon atoms in which each of the hydrogen atoms may be independently replaced by halide, R¹⁴ is aryl or a straight or

branched C₁-C₂₀ alkyl group, and where an N(R¹⁴)₂ group is present, the two R¹⁴ groups may be joined to form a 5- or 6-membered heterocyclic ring; and R¹¹, R¹² and R¹³ are each independently selected from the group consisting of H, halogen, C₁-C₂₀ alkyl, C₃-C₈ cycloalkyl, C(=Y)R⁵, C(=Y)NR⁶R⁷, COCl, OH, CN, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl oxiranyl, glycidyl, aryl, heterocyclyl, aralkyl, aralkenyl, C₁-C₆ alkyl in which from 1 to all of the hydrogen atoms are replaced with halogen and C₁-C₆ alkyl substituted with from 1 to 3 substituents selected from the group consisting of C₁-C₄ alkoxy, aryl, heterocyclyl, C(=Y)R⁵, C(=Y)NR⁶R⁷, oxiranyl and glycidyl; where R⁵ is alkyl of from 1 to 20 carbon atoms, alkoxy of from 1 to 20 carbon atoms, aryloxy or heterocycloxy; and R⁶ and R⁷ are independently H or alkyl of from 1 to 20 carbon atoms, or R⁶ and R⁷ may be joined together to form an alkylene group of from 2 to 5 carbon atoms, thus forming a 3- to 6-membered ring; such that no more than two of R¹¹, R¹² and R¹³ are H.

126. (New): The macroinitiator of claim 90, wherein the polymer block is a polydimethylsiloxane polymer block.